

**Unsaturated Carbosilane and Carbosiloxane Polymers  
Possessing the Reactive Si-Cl Bond**

*FINAL REPORT*

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13. ABSTRACT (Maximum 200 words)

The objective of this research has been broadened from simply producing a highly solvent resistant thermoplastic elastomer for military use to producing a polymer backbone that can be used both as an elastomer as well as for other materials. The idea is to create a "common denominator polymer backbone" that can be applied in many ways. Specifically, the intent is to improve upon existing materials such as butyl rubber in terms of processability, recyclability, durability and elasticity.

Broadening the scope of this reaction would streamline the Army's materials inventory. Potential applications such as mounting structures for military vehicles, conformable seals, flexible fuel cells and the like are all possible applications for this chemistry

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Enclosure 1

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From a technical viewpoint, there are three important points to stress. They are:

1. We have demonstrated successfully the concept of latent reactivity on the backbone of carbosilane polymers.
2. We understand how the reactivity of the silicon methoxy bond and the silicon chlorine bond can be altered in order to produce materials of interest to us.
3. We now understand what materials can be produced using this chemistry and are working towards that end.

**1. Description of the research problem studied, especially the scientific goals as they relate to the Army.** The objective of this research has been broadened from simply producing a highly solvent resistant thermoplastic elastomer for military use to producing a polymer backbone that can be used both as an elastomer as well as for other materials. The idea to create a "common denominator polymer backbone" that can be applied in many ways. Specifically, the intent is to improve upon existing materials such as butyl rubber in terms of processability, recyclability, durability and elasticity.

Broadening the scope of this reaction would streamline the Army's materials inventory. Potential applications such as mounting structures for military vehicles, comformable seals, flexible fuel cells and the like are all possible applications for this chemistry.

**2. Description of the scientific progress and accomplishments.** Three areas of activity have been successfully explored during the last year. All of them are focused on materials have a wide range of temperature stability, that being from - 60°C to 400°C.

First, we have successfully demonstrated the concept of latent reactivity in carbosilane backbone materials. It is an important concept since it allows one to vary the behavior of the resultant material by changing the concentration of latent reactive groups in the backbone of such a polymer. This latent reactivity (based on the methoxy group) permits us to synthesize linear polymers which then can be shaped into the appropriate material of interest for military application. Once shaping is complete, then the latent reactivity is initiated leading to a thermoset having the durability sought. This durability results in either solvent resistant elastomers or high strength plastics depending upon the degree of latent reactivity that is present.

In working through these reaction parameters we have begun to understand the need for improving the crosslink density in such materials, regardless of whether they are intended to be elastomers or high Tg plastics. This observation leads us to sol gel chemistry. We now are probing this catalysis subject further.

Second, the fundamental understanding we have developed regarding the reactivity of both the silicon-methoxy group and the silicon-chlorine group allows us to vary the materials behavior at will. It has been a long process to understand the reactivity of the silicon-chlorine bond. This

first contribution to the chemical literature will not only be important from our point of view, but many others as well.

We have discovered ways of producing highly pure monomers that were not possible before, monomers possessing both the methoxy latent reactive group as well as the silicon chlorine group. At this point we are converting these monomers to polymers.

**Third**, we are advancing the latent concept to include four sites of reactivity in each repeat unit rather than just two. These additional sites of reactivity come about by producing monomers that possess four methoxies per diene rather than two, and four silicon chlorine bonds per diene, rather than two. Synthesis of such monomers represents a challenge, yet our first work suggests that it can be done through statistically selected reactions. Increasing the number of reactive sites per monomer unit has obvious advantages for it allows one to increase crosslink density almost instantaneously.

**Finally**, we remain intrigued by the remarkable thermal stability that these polymers demonstrate. While this stability is a direct reflection of step polymerization chemistry and is not much different from that found for nylon and polyester from that point of view, the thermal stability that is demonstrated is greater than both of these conventional materials. Frankly, we don't understand the reasons for this but we are convinced that the data are correct.

### **3. Technology Transfer:**

**a. Have you given or are you preparing to give samples, data, or a process to the Army or industry for evaluation or use?** We provided samples during our visit to the Aberdeen Proving Ground labs in January and these samples are available if needed. Note that we still need to improve the crosslink density in these materials. This can be done via catalyzed sol gel chemistry.

**b. Names and organization of all those in government to whom you have sent reports and publications.** We have sent financial reports to the people that have been suggested to us. We have also established contacts with people at the Aberdeen Proving Ground, and will keep them informed with reports as suggested.

**c. Are there interactions with other ARO PI's?** We are beginning to interact with Prof. Jean Frechet at Berkeley. Prof. Frechet will come to the University of Florida as a Butler Lecturer in the fall and will be here at least a month. This lectureship series is patterned after that at Cornell University, and with his presence here we intend to gather his views.

I also visited Prof. Harry Allcock at Penn State to present a seminar there as well as to gather his insight in terms of nucleophilic substitution on inorganic polymer backbones. Prof. Allcock is the world's leading authority in this kind of chemistry, so his point of view always helps us in what we are attempting to do. He enjoyed hearing about the latent reactivity concept and supports it fully.

**d. Have there been any interactions with the Army, DoD, or industry such as research results transfer, research discussion or personal meetings going beyond "C" above?** Dr. Kiserow is aware of our contacts with Aberdeen Proving Ground and we intend to pursue them as needed. Some of the ideas that I passed along to them during that visit are not directly related to the ARO research we do here, yet at the same time these additional interactions can be beneficial to the Army. To be more specific, the ideas associated with improving the hydrophilic stability of polyurethanes used in collapsible fuel cells might merit further attention. I am attempting to make a connection for Paul Tuchet with Materia, inc. in Pasadena. Materia is the most likely organization to produce the hydrophobic soft phases that he needs. I will keep you and Paul informed on this subject.

Further, we maintain our relationships with Dow Chemical such that when it comes time to scale up the latent crosslinkable silicon-based polymers for evaluation, we can go to them for help. Eventually they could become the supplier of these materials on a large scale for Army needs.

**e. Were there any breakthroughs such as developing a new instrument, technique, or process that may significantly impact your own or others' research or industry?** The most important concept that has been developed in the most recent funding period has been that of latent reactivity of a carbosilane backbone. There is no question that the concept is valid.

We remain very enthusiastic about what it can mean in terms of materials development. The need here is to better understand catalysis of the crosslinking reaction itself, to determine the appropriate number of reactive sites per repeat unit, and to apply these principles to specific materials development. The question now becomes what materials are of interest to the Army besides solvent resistant thermoplastic elastomers? Once we have a better feel for this, we can target those sorts of polymers as well.

**f. Do you have any interesting samples or items to be used for demonstration of some aspect of your research or result?** The samples that we showed during our visit to the Aberdeen Proving Ground Laboratory are available for your use. My advice is that we wait until we have improved crosslink density before we begin showing them broadly however.

**g. Have any of your students gone to work permanently or temporarily for the ARO or DoD during the current grant?** As you know, Dr. Jim Pawlow expressed interest in the position available at the Aberdeen Proving Ground Laboratory and we are pursuing this now.

**h. Has anyone given you manpower, supplies, samples, equipment, information or research funds that are leveraged in any way for the ARO effort?** We interact with the National Science Foundation to gain relevant information regarding catalysis used in producing the latent reactivity backbone polymer. This catalyst research is essential to producing the polymers that we need and this will continue.

In addition, we intend to seek advice relevant to sol gel catalysis. Dr. Larry Hench developed these concepts quite extensively while here at the University of Florida in the Materials Science Department to produce monolithic glass. Larry and I have known each other for quite some time

and I will get in touch with him in the next few weeks regarding this. Presently, he holds a chaired professorship at Imperial College in London.

**4. List of manuscripts with titles and journal names for all manuscripts submitted or published with ARO support during the last year.**

**ARO Publications During This Reporting Period:**

1. Brzezinska, K. R.; Wagener, K. B. and Burns, G. T., *J. Polym. Sci., Part A.*, **37**, 849 (1999).
2. Brzezinska, K. R.; Schitter, R. and Wagener, K. B., *J. Polym. Sci., Part A*, submitted (1999).
3. Brzezinska, K. R.; Wagener, K. B. and Burns, G. T., Silicones and Silicone-Modified Materials, ACS Sym. Ser., accepted (1999).
4. Wagener, K. B.; Brzezinska, K. R. and Schitter, R., *Polymer Preprints*, **40**(2), 962 (1999).
5. Cummings, S. K.; Anderson, J. D.; Pawlow, J. H. and Wagener, K. B., *Polymer Int.*, submitted (1999).
6. Church, A. C.; Pawlow, J. H. and Wagener, K. B., *Polymer Preprints*, **40**(1), 129 (1999).
7. Church, A. C.; Master's Thesis, University of Florida, "Examination of the Substitution Chemistry of Dialkyldichlorosilanes", 1999.

**ARO Presentations During This Reporting Period:**

8. K. B. Wagener and J. H. Pawlow, "Acyclic Diene Metathesis Polymerization as a Route to Substituted Carbosilane Elastomers", National American Chemical Society Meeting, PMSE Division, Anaheim, CA, Mar. 21-25, 1999.
9. A. C. Church, J. H. Pawlow and K. B. Wagener, "Synthesis of Substituted Bis(Alkenyl)silanes for Use in ADMET Polymerization", National American Chemical Society Meeting, Polymer Division, Anaheim, CA, Mar. 21-25, 1999.
10. J. H. Pawlow, A. C. Church and K. B. Wagener, "ADMET Synthesis of Substituted Poly(carbosilanes)", International Symposium on Metathesis and Related Chemistry, Kerkrade, The Netherlands, July 11-15, 1999.
11. K. B. Wagener, K. R. Brzezinska and R. Schitter, "Cross-Linkable Homopolymers and Copolymers by ADMET Chemistry", National American Chemical Society Meeting, New Orleans, LA, August 1999.

**5. List of scientific personnel supported and honors and awards received. Principals contributing to the project during this reporting period are:**

1. Dr. Jim Pawlow, postdoctoral associate from Penn State University. Jim continues to make important

contributions as mentioned above. He has expressed interest in working for the Army Research Laboratory.

2. Cameron Church, graduate student, University of Florida. Cameron has successfully defended her oral proposal and is continuing on for the Ph.D. I anticipate her graduation within one-two years.
3. Dr. Krystyna Brzezinska, Polish Academy of Sciences. Krystyna has received her green card now and presently is employed by the University of California, Santa Barbara. She has been there since October of last year.
4. Dan Koren, undergraduate, University of Florida. Dan has just joined us and is working in the synthesis area specifically under Dr. Pawlow's guidance. He is a very enthusiastic young man and plans to attend graduate school in chemistry

Thus, the Army's mission of serving educational needs while developing new technology is being met in this project. I expect you are pleased with this as well.

Honors during the past year include my being selected for induction in the Clemson Academy of Engineers and Scientists. There are only 20 members of this Academy, starting with the founder of Clemson University, Thomas Green Clemson. I was one of the first two chemists to be selected for this honor.

Regarding cash flow, all of the ARO funds have been expended for this research project.